

# Bulk fluid phase behaviour of colloidal platelet-sphere and platelet-polymer mixtures

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## Abstract

Using a geometry-based fundamental measure density functional theory, we calculate bulk fluid phase diagrams of colloidal mixtures of vanishingly thin hard circular platelets and hard spheres. We find isotropic-nematic phase separation with strong broadening of the biphasic region upon increasing the pressure. In mixtures with large size ratio of platelet and sphere diameter, there is also demixing between two nematic phases with differing platelet concentrations. We formulate a fundamental-measure density functional for mixtures of colloidal platelets and freely overlapping spheres, which represent ideal polymers, and use it to obtain phase diagrams. We find that for low platelet-polymer size ratio in addition to isotropic-nematic and nematic-nematic phase coexistence, platelet-polymer mixtures also display isotropic-isotropic demixing. In contrast, we do not find isotropic-isotropic demixing in hard core platelet-sphere mixtures for the size ratios considered.

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## I. INTRODUCTION

Understanding the equilibrium properties of colloidal systems and the relationship between the microscopic properties, such as particle shapes and sizes, and the macroscopic properties of a dispersion is essential for the task of creating new materials with desired characteristics. Here anisotropic colloids are relevant due to the possible formation of liquid crystalline phases. Among them platelet-like colloids are ubiquitous in nature; gibbsite or certain clays are specific examples.

Despite their simplicity, hard-core models are very suitable candidates to investigate the phase behaviour of colloidal systems. Since Onsager's pioneering work on the isotropic-nematic (*IN*) phase transition in a fluid of rods [1], a wealth of studies has been carried out in order to elucidate the equilibrium properties of anisotropic hard particles, including the fluid of circular platelets with vanishing thickness using Onsager-like theories [2, 3] and fundamental measure theory (FMT) [4, 5]; see Ref. [6] for a recent review of the literature for platelets and Refs. [7–9] for reviews of FMT.

During the last few years, binary colloidal mixtures have received considerable attention. The addition of a second component induces profound changes in the phase diagram with new phenomena arising such as demixing, reentrant phase boundaries, as well as the emergence of phase transitions due to the depletion mechanism. Studies of binary mixtures that involve platelets were conducted for mixtures of thick and thin platelets [10, 11], binary platelets with different diameters [12], and mixtures of platelets and rods [13, 14].

In this paper we use density functional theory (DFT) [15], and in particular a geometry-based fundamental measure free energy functional [4], in order to investigate the bulk fluid properties in mixtures of infinitely thin platelets and hard spheres. Such mixtures have been previously considered by Harnau and Dietrich using DFT [16] and by Oversteegen and Lekkerkerker by means of a free-volume scaled-particle approach [17]. The authors restricted their analyses to isotropic states of platelets. Both studies found coexistence between an isotropic fluid rich in platelets and a solid phase rich in spheres, as well as the stability of a phase transition between two isotropic phases with differing compositions for small values of the platelet-sphere size ratio. Both studies neglect the excluded volume interaction between the platelets, which can certainly be a good approximation if the density of platelets is very low. We will compare to these findings below. We compare also to results from an extended

Onsager theory with Parsons-Lee rescaling [18, 19] which includes two-body correlations only. In contrast, the geometry-based density functional that we use here includes explicitly non-local higher-body correlations. The non-local structure of the free energy functional [4] is specifically tailored for the present shapes. For general convex bodies much recent effort [20–22] was devoted to improve Rosenfeld’s original FMT for non-spherical shapes [23–25].

Here we also study mixtures of platelets and non-adsorbing ideal model polymers [26]. Polymers are modelled following the ideas of Asakura and Oosawa [27], and Vrij [28], i.e., they are treated as fully interpenetrable spheres that cannot overlap with the colloidal platelets. This is to be regarded only as a minimal model, in particular for the platelet-polymer interaction, as both softness and penetrability of a platelet into a polymer coil are neglected. We develop a fundamental measure density functional theory by linearizing the density functional for hard-core mixtures in polymer density [29, 30].

Experimental mixtures of sterically stabilized gibbsite platelets and silica spheres have been studied very recently [31]. The authors found phase separation into platelet-rich and sphere-rich phases, driven by the repulsive interactions between particles of different species. Columnar ordering has been observed in charged mixtures of gibbsite platelets and silica spheres [32, 33]. Furthermore the crystallization of silica spheres in presence of gibbsite platelets (silica-coated) was analyzed in Ref. [34].

The paper is organized as follows. In Sec. II we define the model and outline the DFT. The results are described in section III: mixtures of colloidal platelets and spheres are analyzed in Sec. III A, in Sec. III B we present the results for mixtures of colloidal platelets and ideal polymers, along with a comparison between FMT theory and an extended Onsager theory which is given in III C. Suggestions for future research lines and conclusions are presented in Sec. IV.

## II. MODEL AND THEORY

We consider a binary mixture of  $N_S$  hard spheres with radius  $R_S$  and  $N_D$  hard circular platelets with vanishing thickness and radius  $R_D$ , see Fig. 1 for a schematic illustration. Here and throughout species-dependent quantities are indicated by subscripts  $S$  (spheres) and  $D$  (disks). The pair interaction potential between any two particles is infinite if the particles overlap, and vanishes otherwise.

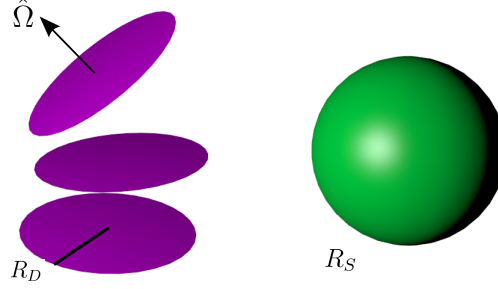


FIG. 1: (Online version in colour.) Schematic representation of the hard core platelet-sphere mixture. The model is a binary mixture of hard spheres of radius  $R_S$  (right) and hard circular platelets of radius  $R_D$  with vanishing thickness (left). The platelet orientation is described by a unit vector  $\hat{\Omega}$  normal to the platelet surface.

### A. Density functional theory for colloidal platelet-sphere mixtures

As is common, we split the Helmholtz free energy functional  $F$  into an ideal-gas part,  $F_{id}$ , and an excess contribution,  $F_{exc}$ . Hence

$$F = F_{id} + F_{exc}. \quad (1)$$

The ideal-gas free energy functional is exactly given by

$$\begin{aligned} \beta F_{id} = & \int d^3r \int d\hat{\Omega} \rho_D(\vec{r}, \hat{\Omega}) [\ln(\rho_D(\vec{r}, \hat{\Omega}) \mathcal{V}_D) - 1] \\ & + \int d^3r \rho_S(\vec{r}) [\ln(\rho_S(\vec{r}) \mathcal{V}_S) - 1], \end{aligned} \quad (2)$$

where  $\beta = 1/k_B T$  is the inverse thermal energy,  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature, and  $\mathcal{V}_i$  is the (irrelevant) thermal volume of species  $i$ . The spatial integral is over the system volume,  $V$ , and the angular integral is over the unit sphere; here  $\hat{\Omega}$  is a unit vector normal to the platelet surface, cf. Fig. 1. The one-body distribution function of platelets is denoted by  $\rho_D(\vec{r}, \hat{\Omega})$ , and that of spheres by  $\rho_S(\vec{r})$ , the latter being trivially independent of orientation due to the rotational symmetry of the spheres. In general both distribution functions depend on position  $\vec{r}$ . In the application to bulk fluid phase behaviour below we consider only homogeneous states, which are independent of  $\vec{r}$ . Without loss of generality we introduce an orientational distribution function for the platelets,  $\Psi_D(\vec{r}, \hat{\Omega})$ , via  $\rho_D(\vec{r}, \hat{\Omega}) = \rho_D(\vec{r}) \Psi_D(\vec{r}, \hat{\Omega})$ . Here  $\rho_D(\vec{r})$  is the number density of platelets, which gives the differential number of platelets with any orientation in the differential volume element at  $\vec{r}$ .

The excess part of the free energy functional,  $F_{exc}$ , that accounts for the excluded volume interactions between all particles, is approximated by a geometry-based density functional, which has the structure

$$\beta F_{exc} = \int d^3r \Phi(\{n_\nu^i\}), \quad (3)$$

where the reduced free energy density,  $\Phi$ , is a function of a set of weighted densities,  $\{n_\nu^i\}$ , where  $i = S, D$  labels the species, and  $\nu$  the type of weight function. The free energy density can be grouped into three different contributions,  $\Phi = \Phi_S + \Phi_D + \Phi_{SD}$ . Here  $\Phi_S$  describes sphere-sphere interactions only. Both  $\Phi_D$  and  $\Phi_{SD}$  describe coupling of spheres and platelets, with  $\Phi_D$  containing the terms that generate the FMT functional for pure platelets [4] in the limit of vanishing density of spheres. In detail, the reduced excess free energy for the interaction between spheres,  $\Phi_S$ , is taken to be of the original Rosenfeld form [23],

$$\begin{aligned} \Phi_S = & -n_0^S \ln(1 - n_3^S) + \frac{n_1^S n_2^S - \vec{n}_{v1}^S \cdot \vec{n}_{v2}^S}{1 - n_3^S} \\ & + \frac{(n_2^S)^3 - 3n_2^S \vec{n}_{v2}^S \cdot \vec{n}_{v2}^S}{24\pi(1 - n_3^S)^2}. \end{aligned} \quad (4)$$

Here and in the following two equations we drop the spatial dependence on  $\vec{r}$  of the weighted densities for the sake of notational convenience. The interactions between platelets are described by

$$\begin{aligned} \Phi_D = & \int d\hat{\Omega} \frac{n_1^{DD}(\hat{\Omega}) n_2^D(\hat{\Omega})}{1 - n_3^S} \\ & + \int d\hat{\Omega} \int d\hat{\Omega}' \frac{n_2^{DDD}(\hat{\Omega}, \hat{\Omega}') n_2^D(\hat{\Omega}) n_2^D(\hat{\Omega}')}{24\pi(1 - n_3^S)^2}. \end{aligned} \quad (5)$$

The first term in Eq. (5) represents the interaction between two platelets. It reduces to the exact second order contribution of the virial series for the free energy of platelets if there are no spheres in the mixture ( $\rho_S = 0$ ). The second term corresponds to the interaction between three platelets (see Ref. [4, 12] for details). The factors proportional to  $(1 - n_3^S)$  in the denominators account for the volume occupied by the spheres in the system.

The further contribution to the reduced excess free energy due to the interaction between

platelets and spheres is

$$\begin{aligned}
\Phi_{SD} = & - \int d\hat{\Omega} n_0^D(\hat{\Omega}) \ln(1 - n_3^S) \\
& + \int d\hat{\Omega} \frac{n_1^S n_2^D(\hat{\Omega}) + n_2^{SD}(\hat{\Omega}) n_1^D(\hat{\Omega}) - \vec{n}_{v2}^{SD}(\hat{\Omega}) \cdot \vec{n}_{v1}^D(\hat{\Omega})}{1 - n_3^S} \\
& + \int d\hat{\Omega} \frac{[n_2^{SD}(\hat{\Omega}) n_2^{SD}(\hat{\Omega}) - \vec{n}_{v2}^{SD}(\hat{\Omega}) \cdot \vec{n}_{v2}^{SD}(\hat{\Omega})] n_2^D(\hat{\Omega})}{8\pi(1 - n_3^S)^2} \\
& + \int d\hat{\Omega} \int d\hat{\Omega}' \frac{n_2^{SDD}(\hat{\Omega}, \hat{\Omega}') n_2^D(\hat{\Omega}) n_2^D(\hat{\Omega}')}{8\pi(1 - n_3^S)^2}.
\end{aligned} \tag{6}$$

All weighted densities are obtained by convolving the density with specific weight functions. For hard spheres the scalar weighted densities are:

$$n_\nu^S(\vec{r}) = w_\nu^S(\vec{r}) * \rho_S(\vec{r}), \quad \nu = 0, 1, 2, 3 \tag{7}$$

and the vectorial weight densities are given by:

$$\vec{n}_\nu^S(\vec{r}) = \vec{w}_\nu^S(\vec{r}) * \rho_S(\vec{r}), \quad \nu = v1, v2, \tag{8}$$

where  $*$  denotes the three-dimensional convolution  $h(\vec{r}) * g(\vec{r}) = \int d^3x h(\vec{x})g(\vec{x} - \vec{r})$ . Here  $w_\nu^S$  and  $\vec{w}_\nu^S$  are the Rosenfeld weight functions for hard spheres [23]:

$$\begin{aligned}
w_3^S(\vec{r}) &= \Theta(R_S - |\vec{r}|), \\
w_2^S(\vec{r}) &= \delta(R_S - |\vec{r}|), \\
\vec{w}_{v2}^S(\vec{r}) &= w_2^S(\vec{r}) \frac{\vec{r}}{|\vec{r}|},
\end{aligned} \tag{9}$$

where  $\Theta(\cdot)$  is the Heaviside step function and  $\delta(\cdot)$  is Dirac's delta distribution. Further weight functions for hard spheres are  $w_1^S(\vec{r}) = w_2^S(\vec{r})/(4\pi R_S)$ ,  $w_0^S(\vec{r}) = w_2^S(\vec{r})/(4\pi R_S^2)$ , and  $\vec{w}_{v1}^S(\vec{r}) = \vec{w}_{v2}^S(\vec{r})/(4\pi R_S)$ .

The sphere-platelet coupling is described by the weighted densities

$$\begin{aligned}
n_2^{SD}(\vec{r}, \hat{\Omega}) &= w_2^{SD}(\vec{r}, \hat{\Omega}) * \rho_S(\vec{r}), \\
\vec{n}_{v2}^{SD}(\vec{r}, \hat{\Omega}) &= \vec{w}_{v2}^{SD}(\vec{r}, \hat{\Omega}) * \rho_S(\vec{r}), \\
n_2^{SDD}(\vec{r}, \hat{\Omega}, \hat{\Omega}') &= w_2^{SDD}(\vec{r}, \hat{\Omega}, \hat{\Omega}') * \rho_S(\vec{r}),
\end{aligned} \tag{10}$$

where the weight functions are

$$\begin{aligned}
w_2^{SD}(\vec{r}, \hat{\Omega}) &= \frac{4}{\pi} \sqrt{1 - (\vec{r} \cdot \hat{\Omega}/R_S)^2} w_2^S(\vec{r}), \\
\vec{w}_{v2}^{SD}(\vec{r}, \hat{\Omega}) &= 4 \frac{\vec{r} - (r \cdot \hat{\Omega}) \hat{\Omega}}{\pi R_S} w_2^S(\vec{r}), \\
w_2^{SDD}(\vec{r}, \hat{\Omega}, \hat{\Omega}') &= \frac{8}{\pi} \left| (\hat{\Omega} \times \hat{\Omega}') \cdot \vec{w}_{v2}^S(\vec{r}) \right|.
\end{aligned} \tag{11}$$

Finally, the weighted densities for platelets are

$$\begin{aligned}
n_\nu^D(\vec{r}, \hat{\Omega}) &= w_\nu^D(\vec{r}, \hat{\Omega}) * \rho_D(\vec{r}, \hat{\Omega}), \quad \nu = 0, 1, 2, \\
\vec{n}_{v1}^D(\vec{r}, \hat{\Omega}) &= \vec{w}_{v1}^D(\vec{r}, \hat{\Omega}) * \rho_D(\vec{r}, \hat{\Omega}), \\
n_1^{DD}(\vec{r}, \hat{\Omega}') &= \int d\hat{\Omega} w_1^{DD}(\vec{r}, \hat{\Omega}, \hat{\Omega}') * \rho_D(\vec{r}, \hat{\Omega}), \\
n_2^{DDD}(\vec{r}, \hat{\Omega}, \hat{\Omega}') &= \int d\hat{\Omega}'' w_2^{DDD}(\vec{r}, \hat{\Omega}'', \hat{\Omega}, \hat{\Omega}') * \rho_D(\vec{r}, \hat{\Omega}''),
\end{aligned} \tag{12}$$

and their corresponding weight functions are

$$\begin{aligned}
w_0^D(\vec{r}, \hat{\Omega}) &= \frac{1}{2\pi R_D} \delta(R_D - |\vec{r}|) \delta(\vec{r} \cdot \hat{\Omega}), \\
w_1^D(\vec{r}, \hat{\Omega}) &= \frac{1}{8} \delta(R_D - |\vec{r}|) \delta(\vec{r} \cdot \hat{\Omega}), \\
\vec{w}_{v1}^D(\vec{r}, \hat{\Omega}) &= \frac{\vec{r}}{R_D} w_1^D(\vec{r}, \hat{\Omega}), \\
w_2^D(\vec{r}, \hat{\Omega}) &= 2\Theta(R_D - |\vec{r}|) \delta(\vec{r} \cdot \hat{\Omega}), \\
w_1^{DD}(\vec{r}, \hat{\Omega}, \hat{\Omega}') &= \frac{2}{R_D} \left| \hat{\Omega} \cdot (\hat{\Omega}' \times \vec{r}) \right| w_1^D(\vec{r}, \hat{\Omega}), \\
w_2^{DDD}(\vec{r}, \hat{\Omega}, \hat{\Omega}', \hat{\Omega}'') &= \frac{8}{\pi} \left| \hat{\Omega} \cdot (\hat{\Omega}' \times \hat{\Omega}'') \right| w_2^D(\vec{r}, \hat{\Omega}).
\end{aligned} \tag{13}$$

The density functional described here is a special case of the functional for ternary platelet-sphere-needle mixtures [4]. It includes contributions up to third-order in platelet density. It reduces to the original Rosenfeld functional [23] in the case of a monodisperse fluid of hard spheres, and gives results that are in good agreement with Monte Carlo simulation data when describing the monodisperse fluid of vanishingly thin platelets [4, 12, 35]. Hence we are confident that it can be applied successfully to the study of binary mixtures of hard spheres and platelets.

## B. Density functional theory for mixtures of colloidal platelets and ideal polymers

We use a model [26] similar in spirit to the colloid-polymer model of Asakura and Oosawa [27], and Vrij [28], to study a mixture of colloidal platelets, which are as above taken as infinitely thin circular disks, and ideal polymers. The polymers are modeled by fully interpenetrable spheres of radius  $R_P$ . These model polymers cannot overlap with the platelets. We obtain an approximation for the free energy of this system by linearizing the excess part of the free energy for the corresponding hard core system. This strategy follows the derivation of the FMT for the Asakura-Oosawa model from a corresponding binary hard sphere

mixture [29, 30]. Hence we apply the linearization to the hard core functional of Sec. III A in order to obtain a free energy functional for the polymer-platelet mixture,  $F_{exc}^{PD}$ , via

$$F_{exc}^{PD}[\rho_D, \rho_P] = F_{exc}[\rho_D, \rho_S = 0] + \int d^3r \left. \frac{\delta F_{exc}}{\delta \rho_S(\vec{r})} \right|_{\rho_S=0} \rho_P(\vec{r}), \quad (14)$$

where  $\rho_P(\vec{r})$  is the one-body polymer density distribution and  $F_{exc}$  is the free energy functional for the hard core mixture, given in Eq. (3).  $F_{exc}^{PD}$  can be expressed in terms of a reduced free energy density

$$\beta F_{exc}^{PD} = \int d^3r \Phi_{PD}(\{n_\nu^i\}), \quad (15)$$

where the reduced free energy,  $\Phi_{PD}$ , is a simple expression linear in polymer density and with up to cubic contributions in platelet density:

$$\begin{aligned} \Phi_{PD} = & \int d\hat{\Omega} n_0^D(\hat{\Omega}) n_3^P(\hat{\Omega}) \\ & + \int d\hat{\Omega} \left( n_1^P(\hat{\Omega}) n_2^D(\hat{\Omega}) + n_2^{PD}(\hat{\Omega}) n_1^D(\hat{\Omega}) - \vec{n}_{v2}^{PD}(\hat{\Omega}) \cdot \vec{n}_{v1}^D(\hat{\Omega}) \right) \\ & + \int d\hat{\Omega} \int d\hat{\Omega}' \frac{n_2^{PDD}(\hat{\Omega}, \hat{\Omega}') n_2^D(\hat{\Omega}) n_2^D(\hat{\Omega}')}{8\pi} \\ & + \int d\hat{\Omega} n_1^{DD}(\hat{\Omega}) n_2^D(\hat{\Omega}) (1 + n_3^P) \\ & + \int d\hat{\Omega} \int d\hat{\Omega}' \frac{n_2^{DD}(\hat{\Omega}, \hat{\Omega}') n_2^D(\hat{\Omega}) n_2^D(\hat{\Omega}')}{24\pi} (1 + 2n_3^P). \end{aligned} \quad (16)$$

We have suppressed the spatial dependence of the weighted densities in the above expressions. The weighted densities that depend on the polymer density (denoted by the letter  $P$  in the superscript) are those for hard spheres (7) and (8), but replacing the hard sphere colloid density,  $\rho_S(\vec{r})$ , by the polymer density  $\rho_P(\vec{r})$ , and replacing the colloid radius,  $R_C$ , by the polymer radius  $R_P$ .

### C. Spatially homogeneous fluids

In the following we restrict ourselves to considering spatially homogeneous fluid states. We use the sphere-platelet model, the expressions for the polymer-platelet model being analogous. The density distributions are independent of the spatial coordinates and

$$\begin{aligned} \rho_S(\vec{r}) &= \rho_S = \text{const}, \\ \rho_D(\vec{r}, \hat{\Omega}) &= \rho_D \Psi_D(\hat{\Omega}), \text{ where } \rho_D = \text{const} \end{aligned} \quad (17)$$



The total number of spheres,  $N_S$ , and that of platelets,  $N_D$ , are obtained by integrating the number densities over the system volume

$$\begin{aligned} N_S &= \int d^3r \rho_S, \\ N_D &= \int d^3r \rho_D. \end{aligned} \tag{18}$$

Eq. (18) implies that the orientational distribution function of platelets is normalized according to

$$\int d\hat{\Omega} \Psi_D(\hat{\Omega}) = 1, \tag{19}$$

which is a different convention compared to that of Ref. [4]. As we do not expect biaxial arrangements of the platelets to occur in bulk, we take the orientational distribution function to depend only on the polar angle  $\theta$  with respect to the nematic director, hence  $\Psi(\hat{\Omega}) = \Psi(\theta)$ . We use a parameter,  $\Lambda$ , and prescribe the functional form of the orientational distribution function as

$$\Psi_D(\theta) = \frac{\exp[\Lambda P_2(\cos \theta)]}{\int d\hat{\Omega} \exp[\Lambda P_2(\cos \theta)]}, \tag{20}$$

satisfying by construction the normalization condition (19). Here  $P_2(\cdot)$  is the second Legendre polynomial, and  $\Lambda$  determines the degree of orientational order of the platelets. For isotropic states  $\Psi_D(\theta) = 1/4\pi$  is obtained for  $\Lambda = 0$ . We characterize the orientational order of the platelets by  $S_D$ , the standard nematic order parameter:

$$S_D = \int d\hat{\Omega} \Psi_D(\theta) P_2(\cos \theta). \tag{21}$$

We have tested the quality of the parameterization (20) by computing the *IN* phase transition of the monodisperse fluid of platelets, and comparing the coexisting densities and order parameter to those obtained from free minimization [4]. The differences for the coexistence densities between both methods are of the order of 1%, see Table I for a comparison. The value of the nematic order parameter at coexistence,  $S_D^N$ , deviates more strongly from the result of free minimization. However, as its magnitude is unusually small for the pure platelet system, this is a very sensitive quantity, see the discussion in Ref. [12]. For completeness, Table I also gives the results from Onsager theory and from Monte Carlo simulations.

In spatially homogeneous fluids, the weighted densities are obtained by integrating the

$\Psi_D(\theta)$	$\rho_D^I R_D^3$	$\rho_D^N R_D^3$	$S_D^N$
FMT, free minimization [12]	0.419	0.469	0.533
FMT, parametrization (20)	0.421	0.462	0.489
Monte Carlo [36]	0.460	0.498	0.45 – 0.55
Onsager theory	0.672	0.858	0.801

TABLE I: Coexistence values for the  $IN$  phase transition of a monodisperse fluid of hard circular platelets with vanishing thickness. The values in the first row are from free minimization without an *a priori* form of the orientational distribution function [12]. The second row shows the coexisting values using the parameterization (20). Monte Carlo data [36] are presented in the third row. In the fourth row the results from Onsager theory are shown; these are identical to Parsons-Lee theory (Sec. II D), as the packing fraction vanishes in the pure system of platelets. Here,  $\rho_D^I$  and  $\rho_D^N$  are the coexistence densities at the  $IN$  transition, and  $S_D^N$  is the nematic order parameter in the coexisting nematic state.

weight functions over the spatial coordinates. For hard spheres:

$$\begin{aligned}
n_0^S &= \rho_S, \\
n_1^S &= R_S \rho_S, \\
n_2^S &= 4\pi R_S^2 \rho_S, \\
n_3^S &= \frac{4}{3}\pi R_S^3 \rho_S, \\
\vec{n}_{v1}^S &= \vec{n}_{v2}^S = 0.
\end{aligned} \tag{22}$$

The mixed weighted densities that couple spheres and platelets are:

$$\begin{aligned}
n_2^{SD}(\hat{\Omega}) &= 4\pi R_S^2 \rho_S, \\
n_{v2}^{SD}(\hat{\Omega}) &= 0,
\end{aligned} \tag{23}$$

$$n_2^{SDD}(\theta, \theta') = \rho_S \int_{-R_S}^{R_S} dz \int_0^{2\pi} d\phi' \begin{cases} 32\pi|t| & \text{if } t^2 > s^2 \\ 64 \left( \sqrt{s^2 - t^2} + t \arcsin \frac{t}{s} \right) & \text{otherwise,} \end{cases} \tag{24}$$

where  $t = z \sin \theta \sin \theta' \sin \phi'$ , and

$$s = \sqrt{R_S^2 - z^2} \sqrt{\sin^2 \theta \cos^2 \theta' + \cos^2 \theta \sin^2 \theta' - 2 \sin \theta \cos \theta \sin \theta' \cos \theta' \cos \phi'}. \tag{25}$$

Due to our normalization (19), Eq. (24) above and Eq. (105) of Ref. [4] differ by a factor  $(4\pi)^2$ . The integrals over the azimuthal angles  $\phi$  and  $\phi'$  have been performed in order to arrive at (24), as only the polar angle with respect to the nematic director is relevant for uniaxial configurations. For platelets the bulk weight functions reduce to

$$\begin{aligned} n_0^D(\hat{\Omega}) &= \rho_D \Psi_D(\hat{\Omega}), \\ n_1^D(\hat{\Omega}) &= \frac{\pi}{4} R_D \rho_D \Psi_D(\hat{\Omega}), \\ n_2^D(\hat{\Omega}) &= 2\pi R_D^2 \rho_D \Psi_D(\hat{\Omega}), \\ \vec{n}_{v1}^D(\hat{\Omega}) &= 0. \end{aligned} \tag{26}$$

Further contributions to the free energy due to the weighted densities  $n_1^{DD}$  and  $n_2^{DDD}$  are the same as given in Eq. (13) and (27) of Ref. [12] to which we refer the reader directly.

The angular integrals were calculated numerically using Gaussian quadrature. We used 2000 roots for the integrals over the azimuthal angle and 25 roots for the integrals in the polar angle. The orientational distribution function does not depend on the azimuthal angle, and hence the integrals over  $\phi$  can be computed and stored for subsequent use. We checked the accuracy of the numerical procedure by computing selected coexisting points with 100 roots for the integrals over the polar angle. The differences were less than 1%.

#### D. Parsons-Lee theory for colloidal platelet-sphere mixtures

Parsons-Lee theory [18, 19] constitutes an approximation where the second virial contribution to the excess free energy is weighted with a prefactor in order to approximate the effects of higher virial contributions. According to Parsons-Lee theory the excess free energy for a spatially homogeneous binary mixture of hard bodies can be written as (see e.g. [37]):

$$\frac{\beta F_{exc}}{V} = \phi(\eta) \sum_{ij} \rho_i \rho_j \int d\hat{\Omega} \int d\hat{\Omega}' \Psi_i(\hat{\Omega}) \Psi_j(\hat{\Omega}') v_{ex}^{ij}(\Omega, \Omega'), \tag{27}$$

where  $v_{ex}^{ij}(\hat{\Omega}, \hat{\Omega}')$  is the excluded volume between two particles of species  $i$  and  $j$  with orientations given by  $\hat{\Omega}$  and  $\hat{\Omega}'$ , respectively. The prefactor  $\phi(\eta)$  depends on the chosen reference system. Here  $\eta$  is the total packing fraction of the mixture  $\eta = \sum_i \rho_i v_i$ , where  $v_i$  is the particle volume of species  $i$ . Our reference system is a pure fluid of hard spheres, and for the present model  $\eta = v_S \rho_S$ , as the platelet volume vanishes. Using the Carnahan-Starling

equation of state, the prefactor in the excess free energy is

$$\phi(\eta) = \frac{4 - 3\eta}{8(1 - \eta)^2}. \quad (28)$$

The orientational distribution function for spheres is  $\Psi_S(\hat{\Omega}) = 1/4\pi$ , and for platelets is given in Eq. (20). The excluded volume between two spheres is

$$v_{ex}^{SS}(\hat{\Omega}, \hat{\Omega}') = \frac{32}{3}\pi R_S^3, \quad (29)$$

between platelets and spheres

$$v_{ex}^{DS}(\hat{\Omega}, \hat{\Omega}') = 2\pi R_S R_D^2 + \pi^2 R_D R_S^2 + \frac{4}{3}\pi R_S^3, \quad (30)$$

and, finally, between two platelets

$$v_{ex}^{DD}(\hat{\Omega}, \hat{\Omega}') = 4\pi R_D^3 \sin \gamma, \quad (31)$$

where  $\gamma$  is the angle between  $\hat{\Omega}$  and  $\hat{\Omega}'$ . For pure platelets  $\eta = 0$ , and hence (28) reduces to  $\phi(\eta) = 1/2$ , which renders (27) identical to the (Onsager) second-virial functional.

### E. Coexistence conditions

In what follows we denote the composition of the mixture,  $x$ , by the molar fraction of hard spheres, *i.e.*,  $x = \rho_S/\rho$ , where  $\rho = \rho_S + \rho_D$  is the total density. The molar fraction of platelets is then simply  $\rho_D/\rho = 1 - x$ . The equilibrium properties of the mixture are obtained by minimizing the Gibbs free energy per particle  $g = F/N_T + p/\rho$  at constant composition  $x$ , pressure  $p$ , and temperature  $T$ . Here  $F$  is the total Helmholtz free energy, and  $N_T = N_S + N_D$  is the total number of particles. We use a standard Newton-Raphson method to minimize  $g$  as a function of  $\rho$  and  $\Lambda$ . Binodal lines are located by a common-tangent construction on  $g(x)$ , which is equivalent to the equality of chemical potentials of both species at the coexisting values of  $x$  and  $\rho$ . Thermal and mechanical equilibrium are satisfied in advance by fixing both temperature and pressure.

Correspondingly, for the platelet-polymer mixture,  $x = \rho_P/\rho$ , and  $\rho = \rho_P + \rho_D$ . The coexistence conditions are those given above with colloidal spheres quantities exchanged by the respective polymer quantity.

### III. RESULTS

The pure fluid of hard platelets with vanishing thickness undergoes a first order  $IN$  phase transition as a function of density. Table I summarizes the values for the coexisting densities and for the nematic order parameter according to the present FMT. The results are in good agreement with Monte Carlo simulation data [38, 39]. Columnar and solid phases appear only in the limit of infinite density in a pure system of platelets with vanishing thickness [36]. In a monodisperse fluid of hard spheres there is a well-known first-order fluid-solid phase transition by increasing the density. We have not studied spatially ordered phases, but give some comments about the stability of spatially homogeneous phases with respect to hard sphere crystallization in Sec. IV.

#### A. Mixtures of colloidal platelets and spheres

In Fig. 2 we present the phase behaviour of mixtures of platelets and spheres for three different mixtures with size ratios  $R_D/R_S = 2$  (first column), 5 (second column), and 10 (third column). We comment on the behaviour for smaller size ratios at the end of the section. In Fig. 2 (a1) we show the phase diagram in the plane of reduced pressure,  $\beta p R_D^3$ , and molar fraction of spheres,  $x$ , for a mixture with size ratio  $R_D/R_S = 2$ . The  $IN$  phase transition in the pure fluid of platelets ( $x = 0$ ) moves to higher pressures and the fractionation becomes stronger when spheres are added to the system. Upon increasing the pressure, the nematic branch of the binodal initially moves to higher compositions, but then bends back on itself approaching  $x = 0$ . The nematic phase is stable only when the molar fraction for spheres is very low.

In Fig. 2 (a2) we plot the phase diagram for the same mixture in the plane of reduced density of disks,  $\rho_D R_D^3$ , and packing fraction of spheres,  $\rho_S v_S$ , where  $v_S$  is the sphere volume. The  $IN$  biphasic region strongly broadens when the packing fraction of spheres in the mixture is increased. The orientational order parameter of platelets,  $S_D$ , along the nematic side of the binodal is shown in panel (a3) of Fig. 2. We also display the total orientational order parameter of the mixture i.e., the nematic order parameter of platelets weighted by the composition of platelets:

$$S_{tot} = \rho_D / \rho S_D = (1 - x) S_D. \quad (32)$$

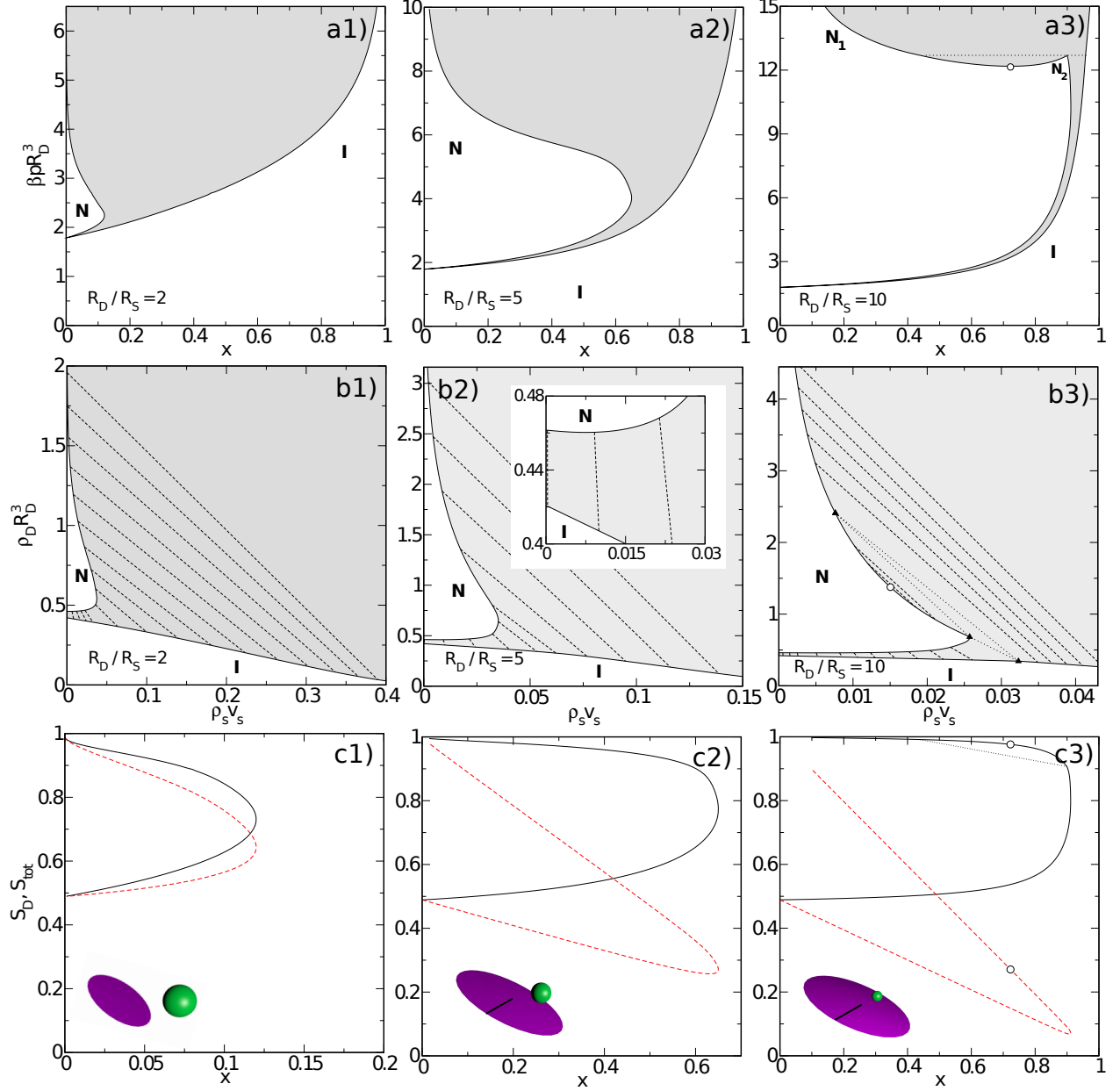


FIG. 2: (Online version in colour.) Phase diagrams of binary mixtures of spheres and platelets with three different values of the platelet-sphere size ratio:  $R_D/R_S = 2$  (first column), 5 (second column), and 10 (third column). For each mixture we show the reduced pressure  $\beta p R_D^3$  vs composition of spheres  $x$  (first row), the reduced density of platelets  $\rho_D R_D^3$  as a function of the packing fraction for spheres  $\rho_S v_S$  (second row), and the nematic order parameters along the nematic side of the binodal (third row). The shadowed areas indicate two-phase regions. Empty circles represent critical points. Dotted lines represent triple points. The dashed lines in the second row are selected tie lines that connect two coexisting points on the binodal. The inset in panel (b2) is a zoom of the region close to the  $IN$  phase transition of the pure fluid of platelets. The solid black (dashed red) lines in the third row represent the platelets' (total) nematic order parameter,  $S_D$  ( $S_T$ ). The insets in the third row are cartons showing the relative size between species.

As the composition of spheres at the  $IN$  phase transition is low, both orientational order parameters are similar to each other, increasing along the nematic side of the binodal.

The second column of Fig. 2 shows the results for mixtures with  $R_D/R_S = 5$ , i.e., for increased relative size of the platelets. The topology of the phase diagrams in both representations is the same than in the above mixture. The main difference to the case of  $R_D/R_S = 2$  is the strongly increased range of compositions for which the nematic phase is stable. For example, in Fig. 2 (a2) one can observe that, for a range of pressures, it is possible to find a stable nematic phase even if the composition of the mixture is  $x \gtrsim 0.6$ . The mechanism that induces the  $IN$  phase transition is different at low and at high pressures. At low pressures the transition is mainly due to the gain in configurational entropy of the platelets in the nematic phase, as the excluded volume between two platelets is minimal if they are parallel to each other. In this regime there is low partitioning between the isotropic and nematic phases. At high pressures, however, the transition is driven by the (unfavourable) excluded volume interactions between platelets and spheres. As a result there is strong demixing between a nematic phase rich in platelets and an isotropic phase mostly composed of spheres.

We focus next on the behaviour of  $\rho_D$  along the nematic branch of the binodal. For low size ratios it monotonically increases as spheres are added to the mixture; but for  $R_D/R_S \gtrsim 2$ ,  $\rho_D$  slightly decreases when the packing fraction of spheres is low (see the inset in panel (b2) of Fig. 2). This behaviour appears to be counterintuitive. However a reduction of the density of platelets at which the nematic phase is stable in the mixture has recently been observed in sedimentation experiments on sterically stabilized mixtures of gibbsite platelets and silica spheres [31] of size ratio  $\approx 6$ . However, the authors found a much stronger effect than that obtained in our theory. The quantitative difference could be due to the influence of gravity on the bulk phase diagram [40]. The polydispersity of the components, the finite thickness of the platelets, and further interactions between the particles (not purely entropic as we are considering here) in the experimental setup could also be relevant to explain the quantitative differences.

The last column in Fig. 2 shows results for the phase behaviour of a mixture with size ratio  $R_D/R_S = 10$ . A prominent alteration of the topology of the phase diagram is that in addition to the  $IN$  phase transition, there is also demixing between two nematic phases with differing compositions. The nematic-nematic phase coexistence region is bounded by a lower critical point and merges with the  $IN$  phase transition at an isotropic-nematic-nematic

triple point. At pressures above the triple point pressure there is strong demixing between an isotropic phase rich in spheres and a nematic phase mostly composed of platelets. The nematic-nematic demixing can be viewed as being driven by a depletion attraction induced between the platelets by the small spheres.

The behaviour of the orientational order parameters along the binodal is shown in the third row of Fig. 2. For small size ratios, panel (c1), both the order parameter of platelets,  $S_D$ , and the total order parameter,  $S_{tot}$ , increase along the nematic branch of the binodal. However, in mixtures where the size ratio is high (panels (c2) and (c3) of Fig. 2)  $S_D$  monotonically increases along the binodal, but the total order parameter,  $S_{tot}$ , first decreases to a minimum and then increases. This qualitative difference may be observable experimentally.

The phase diagram of mixtures with size ratios  $R_D/R_S < 2$  (not shown) are qualitatively similar to the results for  $R_D/R_S = 2$ . In particular, the topology remains unchanged and only *IN* phase separation occurs. This is in contrast to previous studies of mixtures of infinitely thin platelets and hard spheres [16, 17], which reported isotropic-isotropic (*II*) demixing if the size ratio of the mixture is small. In our DFT treatment, we do not find *II* coexistence in the range of size ratios  $0.2 \leq R_D/R_S \leq 10$ .

## B. Mixtures of colloidal platelets and ideal polymers

We turn to the analysis of mixtures of colloidal platelets and ideal model polymers. Bates and Frenkel studied such mixtures using Monte Carlo simulations and perturbation theory [26]. Following the ideas of Asakura, Oosawa and Vrij [27, 28], the polymers are modelled as freely interpenetrable spheres that cannot overlap with the platelets due to hard repulsion between the unlike species. A DFT for such mixture is obtained by linearizing the excess free energy, Eq. (3), around  $\rho_S = 0$  (see Sec. II B for details).

The bulk fluid phase behaviour of mixtures of colloidal platelets and non-adsorbing polymers is depicted in Fig. 3 for three different values of the size ratio  $R_D/R_P$ . The upper row shows the phase diagram in the pressure-composition plane. The polymer fugacity,  $z_P = \exp(\beta\mu_P)/\mathcal{V}_P$ , with  $\mu_P$  the chemical potential of the polymers, as a function of the density of platelets is represented in the lower row. Here the chemical potential of species  $i$  is obtained from  $\partial F/\partial N_i = \mu_i$ . Note that the fugacity is independent of the (hence irrelevant) thermal volume  $\mathcal{V}_P$  because the chemical potential,  $\mu_p$  is shifted according to the particular



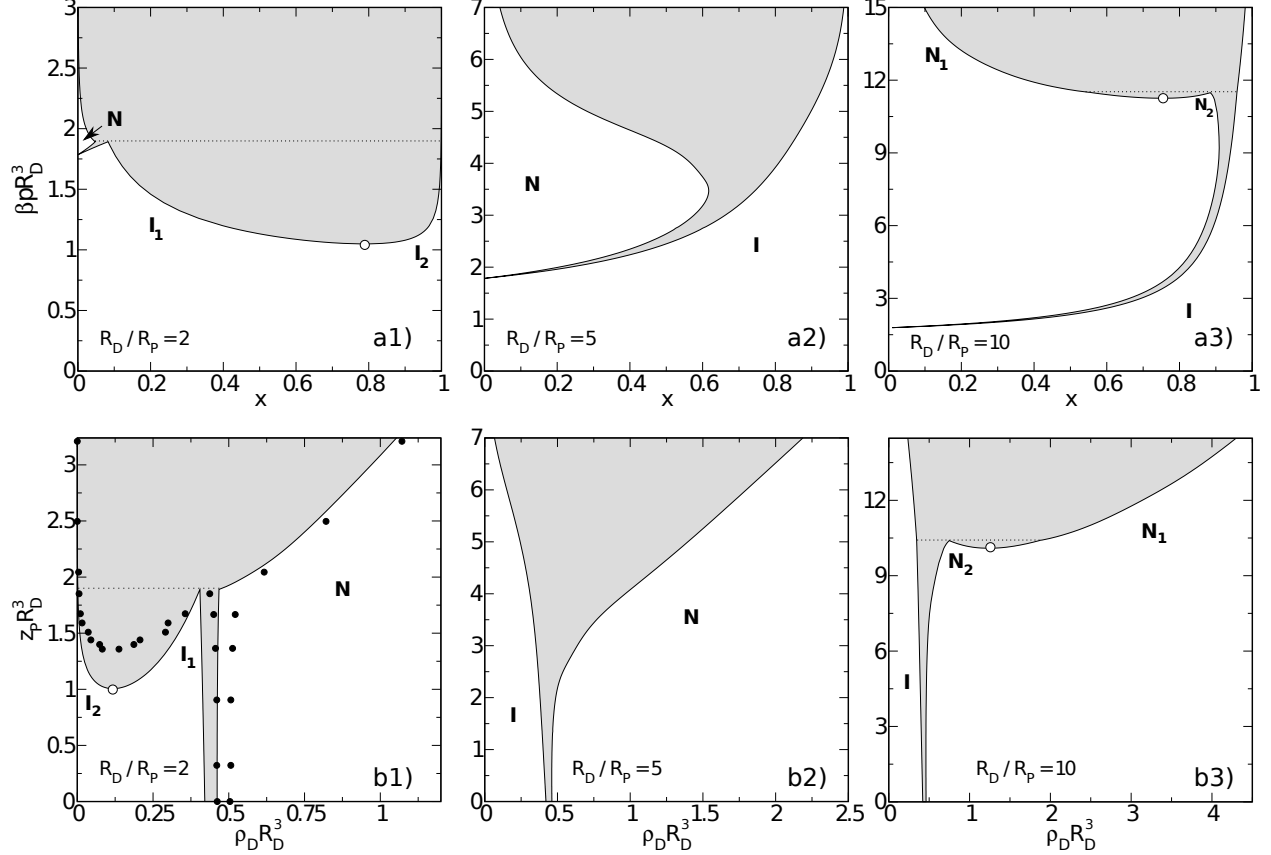


FIG. 3: Phase diagrams of mixtures of colloidal platelets and ideal model polymers for size ratios  $R_D/R_P = 2$  (left),  $R_D/R_P = 5$  (middle), and  $R_D/R_P = 10$  (right). Upper row: pressure,  $\beta p R_D^3$ , as a function of the composition of polymers,  $x$ . Bottom row: fugacity of the polymers,  $z_P R_D^3$ , vs density of platelets,  $\rho_D R_D^3$ . Empty circles present critical points. Dotted lines represent triple points. Full circles in panel (b1) indicate Monte Carlo simulation data [26].

choice of  $\mathcal{V}_P$ .

The main difference to platelet-colloid mixtures is that mixtures of platelets and ideal polymers display prominent demixing between two isotropic states when the size ratio is low enough. In panel (a1) of Fig. 3 we show the results for  $R_D/R_P = 2$ . There is strong demixing between two isotropic phases bounded by a lower critical point. The  $II$  phase separation occurs almost entirely at pressures below the  $IN$  pressure of the pure fluid of platelets. At higher pressures the  $II$  binodal merges with the  $IN$  binodal via a nematic-isotropic-isotropic triple point. This phase diagram differs significantly from that of the hard core mixture with the same size ratio shown in panel (a1) of Fig. 2. The difference between both systems lies in the sphere-sphere excluded volume interactions. In a mixture of platelets and ideal polymers

the gain in accessible volume in the demixed  $II$  state over-compensates the loss of mixing entropy. This is not the case in mixtures of colloidal platelets and spheres for the size ratios considered. It is interesting to note that  $II$  demixing has been found by computer simulation in mixtures of platelets with finite thickness and non-adsorbing polymers [41].

In panel (b1) of Fig. 3 we show a comparison with Monte Carlo simulation data (full circles) [26] for the same mixture ( $R_D/R_P = 2$ ). The agreement is reasonably good, although DFT underestimates the  $IN$  coexisting densities at low polymer concentration and also the fugacity of the polymers along both branches of the  $II$  binodal and hence the location of the critical point. This trend is similar to what was found for the AOV model [42].

The middle (right) column of Fig. 3 shows the phase diagrams of a mixture with size ratio  $R_D/R_P = 5$  ( $R_D/R_P = 10$ ). The behaviour is very similar to the corresponding mixtures of colloidal spheres and platelets, depicted in panels (a2) and (a3) of Fig. 2. Such similarity might be expected because by increasing the relative size of the platelets (in hard-core platelet-sphere mixtures) the platelet-platelet and platelet-sphere interactions dominate over the sphere-sphere interactions. Recall that we do not consider the freezing transition of hard spheres, which would dramatically change the phase behaviour between ideal polymers and colloidal spheres at densities above the freezing transition.

Our results are in qualitative agreement with the experimental observations. For example,  $II$  coexistence has been found in suspensions of sterically stabilized colloidal gibbsite platelets and non-adsorbing polymers (with  $R_D/R_P \approx 2.9$ ) by Lekkerkerker *et al.* [43]. The same study also showed a strong broadening of the  $IN$  two-phase region by increasing the polymer concentration. Nematic-nematic demixing has been recently found [44] in a related system of mixtures of non-adsorbing polymers and positively charged platelets.

### C. FMT vs Parsons-Lee theory

The geometry-based DFT of Sec. II A contains contributions to the excess free energy that are of third order in density. In this section we compare the results from this theory to those from an extended Onsager theory with Parsons-Lee rescaling that explicitly includes only two-body interactions. For details about Parsons-Lee theory, see Sec. II D. The phase diagram of a hard core mixture with size ratio  $R_D/R_S = 2$  according to Parsons-Lee theory is depicted in Fig. 4. It is to be compared with panels (a1) and (b1) of Fig. 2, where

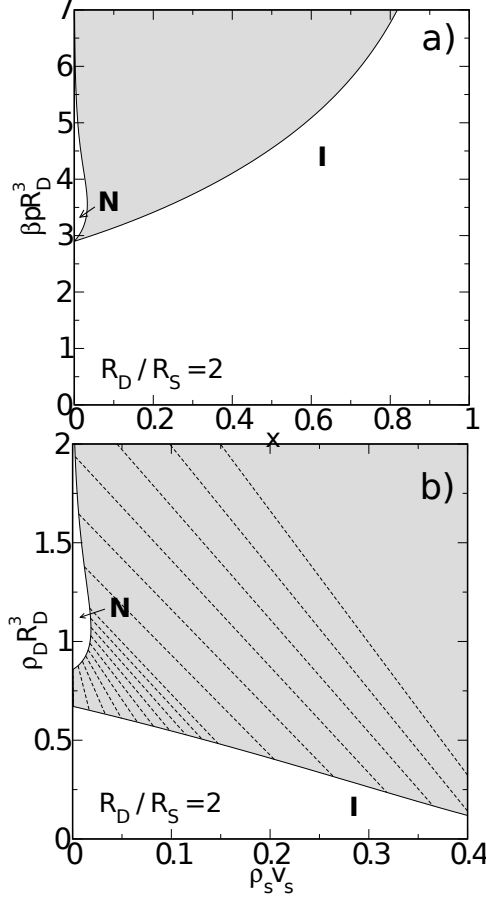


FIG. 4: Bulk phase diagrams of a colloidal mixture of platelets and spheres according to Parsons-Lee theory. (a) Scaled pressure  $\beta p R_D^3$  vs composition of spheres  $x$ . (b) Density of platelets  $\rho_D R_D^3$  as a function of the packing fraction of spheres  $\rho_S v_S$ . The size ratio is  $R_D/R_S = 2$ .

corresponding results obtain from FMT are shown. An immediately noticeable difference is in the location of the  $IN$  phase transition in the pure fluid of platelets. In this limit ( $x = 0$ ) Parsons-Lee theory gives an unchanged result as compared to Onsager theory due to the vanishing packing fraction in the pure fluid of platelets. Hence Parsons-Lee theory clearly overestimates the coexisting densities ( $\rho_D^I R_D^3 = 0.67$  and  $\rho_D^N R_D^3 = 0.86$ ). It also predicts a much too high nematic order parameter at the  $IN$  coexistence,  $S_N = 0.80$  (not shown), compared to FMT and MC simulation.

For  $R_D/R_S = 2$  the topology of the phase diagram predicted by both theories is the same. According to Parsons-Lee theory the partitioning between isotropic and nematic phases is higher than in FMT. A similar trend was observed comparing the current FMT and Onsager theory in binary mixtures of hard platelets with different radius [12]. Parsons-Lee theory

predicts demixing between two nematic phases in mixtures with high size ratio, as does FMT. However, the minimal size ratio for phase segregation to occur between two nematics (using Parsons-Lee theory) is  $R_D/R_S \gtrsim 15$ , considerably higher than the threshold for FMT, which is  $R_D/R_S \approx 10$ . One important difference is that Parsons-Lee theory predicts *II* demixing for low size ratios  $R_D/R_S \lesssim 1$ . Nevertheless, the *II* phase boundary is located at very high pressures and densities and is most likely metastable with respect to segregation between an isotropic phase rich in platelets and a solid phase rich in spheres.

#### IV. CONCLUSIONS

We have investigated the fluid bulk phase behaviour of mixtures of colloidal platelets and spheres using a geometry-based density functional theory [4]. The size ratio  $R_D/R_S$  is the key parameter that controls the behaviour of the system. In mixtures with  $0.2 \leq R_D/R_S \lesssim 10$  we find only *IN* phase separation. We have identified two different mechanisms behind the *IN* phase transition. If the composition of spheres is low, the *IN* transition is driven by the excluded volume interaction between the platelets, similar to the mechanism in a pure fluid of platelets. In this regime, the transition takes place between two phases with low partitioning. As the composition of spheres is increased, the interaction between dissimilar species becomes dominant, and the (unfavourable) excluded volume interactions between spheres and platelets drives strong demixing between an isotropic sphere-rich phase and a nematic platelet-rich phase.

Mixtures with high size ratio,  $R_D/R_S \gtrsim 10$ , also display demixing between two nematics at different compositions. However reliably describing such highly asymmetric mixtures is a very difficult for any theoretical treatment, see the comparison of FMT and simulation results for asymmetric binary hard sphere mixtures [45, 46].

The possible existence of demixing between two isotropic fluids in mixtures of colloidal platelets and spheres remains an open question. The FMT approach does not predict *II* demixing. Previous studies [16, 17] reported *II* phase separation in mixtures where the size of both species is similar. Nevertheless, in both studies the authors neglected excluded volume interactions between platelets. This approximation is valid only if the platelets density is very low. In contrast our theory includes platelet-platelet interactions, modelled via up to cubic contributions in platelet density to the free energy. The bulk free energy for isotropic

states from the present DFT is the same as that from scaled-particle theory [47], which gives further confidence into our results. Carrying out a careful simulation study in order to shed further light on the existence of *II* demixing in the hard core mixture would be very valuable.

We have not considered spatially inhomogeneous phases in this work. The pure fluid of hard spheres undergoes a fluid-solid phase transitions. The freezing transition, according to Monte Carlo simulations [48, 49], takes place at packing fractions  $\rho_S v_S = 0.49$  for the liquid and 0.54 for the solid (values which are higher than the packing fractions considered in the present work). Hence, we expect our fluid phase diagrams to be stable with respect to freezing of the hard spheres. For low size ratios (smaller than those analysed here) we expect an isotropic-solid demixing region in the phase diagram. Columnar as well as solid phases become relevant in systems of platelets with non-vanishing thickness at sufficiently high densities. Hence, it is possible that nematic-nematic demixing in mixtures with high size ratio will be metastable with respect to columnar ordering. Recent experiments by Lekkerkerker *et al.* on mixtures of charged gibbsite platelets and silica spheres [32, 33] have shown a large isotropic-columnar coexisting region. Columnar ordering has also been studied theoretically in mixtures of board-like platelets and spheres in a cubic lattice [50]. Smectic phases are not very common in discotic liquid crystals, but they could appear in real systems with finite thickness [51]. Recent experiments with mixtures of colloidal gibbsite platelets and spheres [52] show that also glass formation can occur at sufficiently high sphere concentrations.

As our theory is mean-field in character, we expect the location of nematic-nematic critical point to change upon including neglected fluctuations, say in computer simulations. Such (future) work could ascertain the stability of nematic-nematic demixing. Furthermore it would be interesting to consider the stability of the nematic-nematic transition upon altering the platelet-polymer interactions, in order to take into account penetrability of platelets and polymers.

The results presented in this work can form the basis for studies of inhomogeneous platelet-sphere mixtures using DFT, such as the analysis of the effects of gravity [53], as

well as wetting and confinement effects.

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